

Yttrium passivation of defects in GeO₂ and GeO₂/Ge interfaces

Hongfei Li and John Robertson

Engineering Dept, Cambridge University, Cambridge, CB2 1PZ, UK

Abstract: Alloying amorphous GeO₂ with Y₂O₃ has been found experimentally to improve its chemical stability and electrical reliability as a gate dielectric in Ge-based field effect transistors. The mechanism is explained here based on density functional calculations. The GeO₂ reliability problem is correlated with oxygen deficiency defects which generate gap states near the band-edges of the underlying Ge. These can be passivated through Y doping. This shifts the defect gap state out of the gap up into the GeO₂ conduction band, thus effectively passivating gap states in the GeO₂ layer.

High mobility channel materials such as Ge, SiGe and InGaAs are of critical importance for the continued scaling of complementary metal oxide semiconductor (CMOS) transistors. Ge, as an elemental semiconductor with larger electron and hole mobilities than Si, would in principle be particularly favored. However, its native oxide GeO₂ and the Ge/GeO₂ interface suffer from worse electronic properties than the Si/SiO₂ interface [1-7], a larger interface trap density (D_{it}), worse electrical reliability [6,7] and unusual oxidation kinetics [8]. At some level, it appears that oxygen deficiency defects occur in GeO₂ for a lower energy cost than in SiO₂ [9].

It is possible that the key defects in SiO₂ and GeO₂ are different. In SiO₂, the main defect is the O vacancy or E' center, and related defects such as the single Si dangling bond. There is also the Si dangling bond on the Si side of the Si/SiO₂ interface (P_b center). In GeO₂, oxygen deficiency is a critical parameter. The Ge^{II} valence state is more stable in GeO_{2-x} than the equivalent Si^{II} in SiO₂, for example the Ge^{II} state is employed in GeO₂ based Bragg gratings [9]. The Ge^{II} state is also notable for the more volatile molecular GeO, which isotope tracer studies show is enabled by O lattice diffusion through the GeO₂ layer [10]. We note that the Ge^{II} oxidation state is widely seen in Ge chemistry, such as in GeSbTe phase change memory materials [11].

In terms of reliability, Lu et al [12,13] recently noted that the addition of group IIIA oxides such as Y₂O₃ into GeO₂ can be beneficial. This reduces the GeO₂ etch rate and GeO evolution rate from GeO₂. The trap density D_{it} and the CV hysteresis are reduced and the electrical reliability is improved. This effect was explained empirically in terms of a more rigid oxide network which led to a lower defect generation rate [13]. However, in gate oxides, reliability is generally attributed to charge trapping at *existing* defects, not the generation of new defects [6,14]. Thus, an atomistic model of the effects would be useful.

Here, we study the electronic structure and energies of the O vacancy and Ge^{II} defects in GeO₂ compared to those in SiO₂ using density functional theory (DFT) calculations. We explain the effect of Y additions in GeO₂, and find that it leads to a passivation effect, expelling defect states out of the GeO₂ band gap. This suggests that the improved reliability of Y doped GeO₂ arises from the passivation of charge traps in GeO₂. The overall effect is compared to that of La, Y or N dopants on O vacancy behavior in HfO₂ where defect states are expelled from the gap so that the electronic structure reverts to the more stable closed-shell configuration.

Our simulations are carried out using the plane-wave, density functional code CASTEP [15], using norm-conserving pseudopotentials with a plane-wave cutoff energy of 750 eV. A Γ point averaging scheme is chosen in all calculations due to the large supercells used. The geometry optimization task

is carried out using the generalized gradient approximation (GGA) for the electronic exchange-correlation functional until the residual force on each atom is below $0.01\text{eV}/\text{\AA}$. The GGA is known to under-estimate the band gap, so the electronic density of states is calculated using the screened exchange hybrid functional [16] to correct the band gap error of GGA.

An amorphous GeO_2 model of 144 atoms was generated by several separate steps. First, a random network of GeO_2 is created by a high temperature molecular dynamics (MD) anneal of crystalline (quartz-like) GeO_2 at 2000 K for 20 ps. It is then cooled down to 300 K in 20 ps. Finally, the system is relaxed to an energy minimum.

We first consider the case of the neutral O vacancy in crystalline (c-) GeO_2 . Creating the vacancy leaves two Ge dangling bonds, which then reconstruct to form a Ge-Ge bond, as in SiO_2 [17], Fig 1(a). The formation energy of the vacancy in oxygen-rich conditions (atmospheric pressure O_2) is given in Table 1. We see that the vacancy formation energy is much greater in SiO_2 than in GeO_2 . Its formation energy in the O-poor condition (the Ge/GeO_2 or Si/SiO_2 equilibrium) is given by subtracting the bulk heat of formation of GeO_2 or SiO_2 per O atom, and is much lower.

The Ge^{II} configuration can be given by a variant of the valence alternation pair (VAP) defects found in chalcogenides. In a covalent random network of a-Se, a VAP consists of an under-coordinated and an over-coordinated atom [18]. A Se-Se bond is broken, and one of the resulting 1-fold coordinated Se sites rebonds to a bulk 2-fold Se site to make it 3-fold site. To do this, the site must become positively charged, then it can form 3 bonds by the 8-N rule. The VAP defect consists of Se_3^+ and Se_1^- , where the subscript denotes coordination number. The VAP is considered to be a low energy defect because the total number of bonds is conserved [16]. VAPs can also exist in binary networks, and have been suggested for SiO_2 [17,19-21] although the vacancy model is generally favored. The VAP is one way to represent the O deficiency of divalent Ge, as explained below.

Starting from the reconstructed O vacancy with a Ge-Ge bond as in Fig 1(a), we break the Ge-Ge bond and flip one of the 3-fold Ge atoms away from the vacancy towards an oxygen atom on its other side to form a new Ge-O bond, Fig. 1(b). This process is shown in Fig 1(b) for crystalline GeO_2 where it is easier to follow, and in Fig 2(a,b) for a random network. For this defect to be consistent with the 8-N rule, the 3-fold O site must become positive as in O_3^+ . Its lost electron transfers to the other 3-fold Ge site to make it Ge_3^- . In the VAP, the 3-fold Ge^- atom is labelled Ge1 in Figs 1(b), 2(b) and the other Ge atom previously at the vacancy is labelled Ge2. The O_3^+ site lies between the sites labelled Ge2 and Ge3. These VAP defects have been studied by Binder et al [22,23] and Li and Lin [24-26].

The partial density of states (PDOS) has been calculated for these defects, using the sX functional. Fig 2(c) shows the PDOS for the Ge-Ge bond across the reconstructed O vacancy in a- GeO_2 . It gives a filled bonding state at 1 eV above the GeO_2 valence band maximum (VBM), and an empty antibonding state at 6.2 eV in the GeO_2 conduction band. These states are aligned to the band edges of the underlying Ge layer in Fig 3 using the conduction band offset of 0.9 eV [26]. We see that these defect states are not so close energetically to the Ge band edges, so they are less critical for charge trapping.

The PDOS of the VAP has two gap states, see Fig 2(d). The gap state at 2.6 eV consists of a filled dangling bond state on the Ge1 site. Its occupied s-like character in Fig 2(b) confirms that Ge1 is in its divalent configuration. We also calculated the relative formation energy of the VAP defect for its neutral and +1 and +2 states, Fig 2(f). The positive state gives the Ge1 site a true dangling bond

character, so the 0/+1 transition in Fig 2(f) lies higher than the PDOS peak in Fig 2(d). The second, empty gap state of the VAP lies at 5.5eV, just below the GeO₂ conduction band edge. This state formally derives from the 3-fold O atom. However, because of the polarity of the Ge-O bonds, this orbital is mostly localised on two adjacent Ge atoms Ge2 and Ge3, Fig. 2(e). These two gap states lie much closer to the band edge energies of Ge itself than those of the O vacancy, as summarised in Fig 3. Thus, these defects act as more effective charge traps, and contribute towards D_{it}. If the VAP defects are located at the interface, they can act as border traps, typically with a broader energy distribution which tails into the Ge gap.

The formation energies of the VAP in SiO₂ and GeO₂ are calculated using supercell models and are given in Table 1. We see that the VAP is ~1.8 eV more expensive than the O vacancy in a-GeO₂, but it is ~3.2 eV more expensive in c-SiO₂. The cost of the vacancy and the VAP become much lower in the O-poor condition, as occurs for example at the Ge/GeO₂ interface. There are also a range of formation energies for defects at the Ge/GeO₂ interface because of the many possible bonding configurations there.

We now consider a GeO₂ alloy in which two Y atoms are substituted for Ge1 and Ge3, the two Ge atoms involved in the VAP, Fig 4(a). We replace the Ge1 and Ge3 atoms by Y, while the Ge2 atom remains unchanged to keep the Y's separate. The network is relaxed. After geometry optimization, the Y replacing 3-fold Ge1 site remains 3-fold, while the Y replacing the 4-fold Ge3 becomes 6-fold coordinated by the formation of extra Y-O bonds to adjacent oxygens. The PDOS of these sites in Fig. 4(b) shows that the defect state on Ge1 previously at 2.6 eV is now removed from the gap, while the defect state at 5.5 eV now moves across to the Ge2 site. Overall, the Y substitution has passivated the hole trap at 2.6 eV by moving this state from the gap into the conduction band, Fig 3(b). Thus, there is no longer a hole trap to lead to the poor reliability.

Now consider the defect passivation mechanism. The defects gave a gap state filled with 2 electrons. Substituting two Ge's with Y's contributes two fewer electrons, so it creates two holes in the valence band. Removing the gap state allows its two defect electrons to fall into the 2 holes in the valence band, regaining a more stable closed-shell configuration, Fig 3(b).

The process is similar to the passivation of O vacancy gap states by two Y or La atoms in HfO₂ [27-29]. There, the neutral vacancy has a state in the upper gap having two electrons. Replacing two Hf's with Y's creates two holes in the valence band. The two electrons previously in that vacancy state drop down into the hole states, thereby forming a closed shell.

The role of the VAP is as follows, from Fig 3 and Table 1. The VAP is not the lowest energy configuration of O-deficit in GeO₂, so the O vacancy is the dominant defect of the two. However, the original O vacancy has a filled state only near the GeO₂ VBM. The energy gain from passivating this would only be the 1 eV per electron as they fall from the Ge-Ge bonding state to the VBM. On the other hand, the filled state of a VAP is much higher, and two electrons falling from this state into the hole states in the VBM release much more energy. Thus, the driving force for passivation is larger. The VAP in GeO₂ acts an intermediate state of higher energy than the vacancy itself, that catalyses the transition from the unpassivated to the passivated state. However, in SiO₂ the VAP is so much higher in energy that it is irrelevant. [The Y atoms are attracted to the VAP in GeO₂ by an energy of order 1 eV, depending on the configuration.](#)

We now consider these effects of Y nearer the Ge/GeO₂ interface. There is now a wide range of possible O vacancy and VAP configurations with a range of energies. A reconstructed O vacancy

next to the interface is actually an interface with a Ge-Ge bond pointing into the GeO_2 side. Thus, this problem could be re-expressed as the condition for the abruptness of the interface. An O vacancy one further layer into the GeO_2 is the next case. This defect could re-arrange into a VAP separated from the interface, or into one now connected to the interface. Substituting Y for Ge's around such defects gives different possibilities. A critical point is that any direct Y-Ge bond with the Ge atom in the Ge layer will give a gap state in the Ge band gap. This is to be avoided. Thus, cases where Y substitutes for Ge atoms in the GeO_2 side are favoured if a beneficial result is desired. We found previously [30] that the advantage of Y (or Sc) over La is that Y favors bonding to O rather than Ge, so that Y will tend to segregate in the oxide, whereas La slightly favors bonding to Ge, so that La segregates into the Ge side.

Many configurations must be checked to give an overall description of the interface case. A useful example is shown in Fig 5(a,b) which shows two substitutional Y's separated from the Ge side, which were separated by a previous O vacancy. This configuration is fully passivated, with no gap states even in the GeO_2 .

In conclusion, we have presented DFT calculations on Y doping of GeO_2 to explain the improved reliability of GeO_2 as a gate dielectric on Ge. It is shown that, the VAP type of O deficiency defect has defect states quite close to the band edges of Ge, which are prone to trap carriers. We find that these gap states can be removed by substituting two Y atoms for Ge atoms at defect site. The passivation mechanism is due to electrons localized at the filled gap state falling to the valence band holes created by Y doping.

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Table 1. Summary of O deficiency defect formation energy (in eV) in bulk SiO₂ crystal, GeO₂ crystal, amorphous GeO₂ and at the Ge/GeO₂ interface in O rich condition. Formation energies in the O-poor condition are found by subtracting the heat of formation of GeO₂ or SiO₂ per oxygen.

| Oxygen deficiency defect type | | c-SiO ₂ | c-GeO ₂ | a-GeO ₂ | Ge/a-GeO ₂ interface |
|-------------------------------|--------|--------------------|--------------------|--------------------|---------------------------------|
| O vacancy | O-rich | 6.14 | 3.16 | 3.04 | 3.05 |
| | O-poor | 1.29 | 0.14 | 0.13 | 0.14 |
| VAP | O-rich | 9.34 | 5.01 | 4.76 | 3.45 |
| | O-poor | 4.49 | 1.99 | 1.85 | 0.54 |

Figure captions

Fig. 1. (a) The reconstructed O vacancy in crystalline GeO₂, (b) the valence alternation pair or VAP, made by inverting the Ge2 site and its bonding to the O. Ge = green, Ge1, Ge2, Ge3 = bright green, O = red, orange = O at VAP.

Fig 2 (a) amorphous GeO₂ with an oxygen vacancy reconstructed as a Ge-Ge bond; (b) PDOS of Ge-Ge bond in GeO₂ from screened exchange; (c) the VAP in a-GeO₂ including the occupied defect state at 2.6 eV, (d) PDOS at the Ge1, Ge2 and Ge3 sites of the VAP in a-GeO₂. (e) the empty defect orbital at +5.2 eV. (f) the relative defect formation energy vs Fermi energy for the Ge1 site of the VAP. Note, the charge on Ge1, or Ge3, is the chemical formal charge, whereas the 0, +1, and +2 is the overall defect charge of the 2-site VAP.

Fig 3. Band alignment of Ge and GeO₂ and the defect levels of (a) the O vacancy, and (b) VAP. (b) also summarises the passivation mechanism of the VAP, following the substitution of Ge by Y, with gap states expelled into the GeO₂ conduction band and the fall of the two electrons at the Ge1 site into the two valence band holes due to this substitution.

Fig 4. (a) Two Y atoms substituted at Ge sites at the VAP in a-GeO₂, (b) PDOS of Y and Ge sites at the VAP in a-GeO₂ calculated by screened exchange; (c) defect orbital at 5.2 eV in the Y substituted VAP. Ge = green, O = red, O at the VAP = orange, Y = light blue.

Fig. 5. (a) Ge/GeO₂ interface where a O vacancy near the interface has been passivated by addition of two Y atoms. Note that they are separated from Ge layer by O bridge bonds. (b) Partial density of states. Note absence of states in the GeO₂ gap.

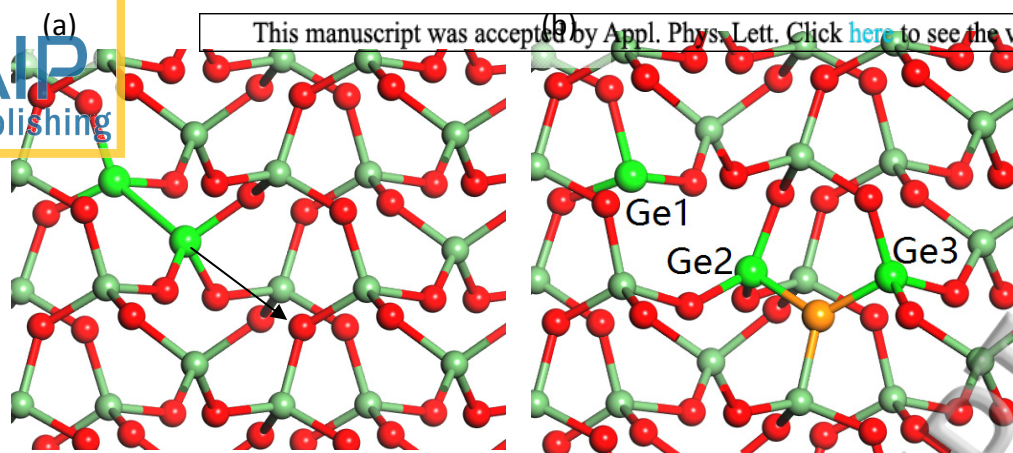


Fig 1

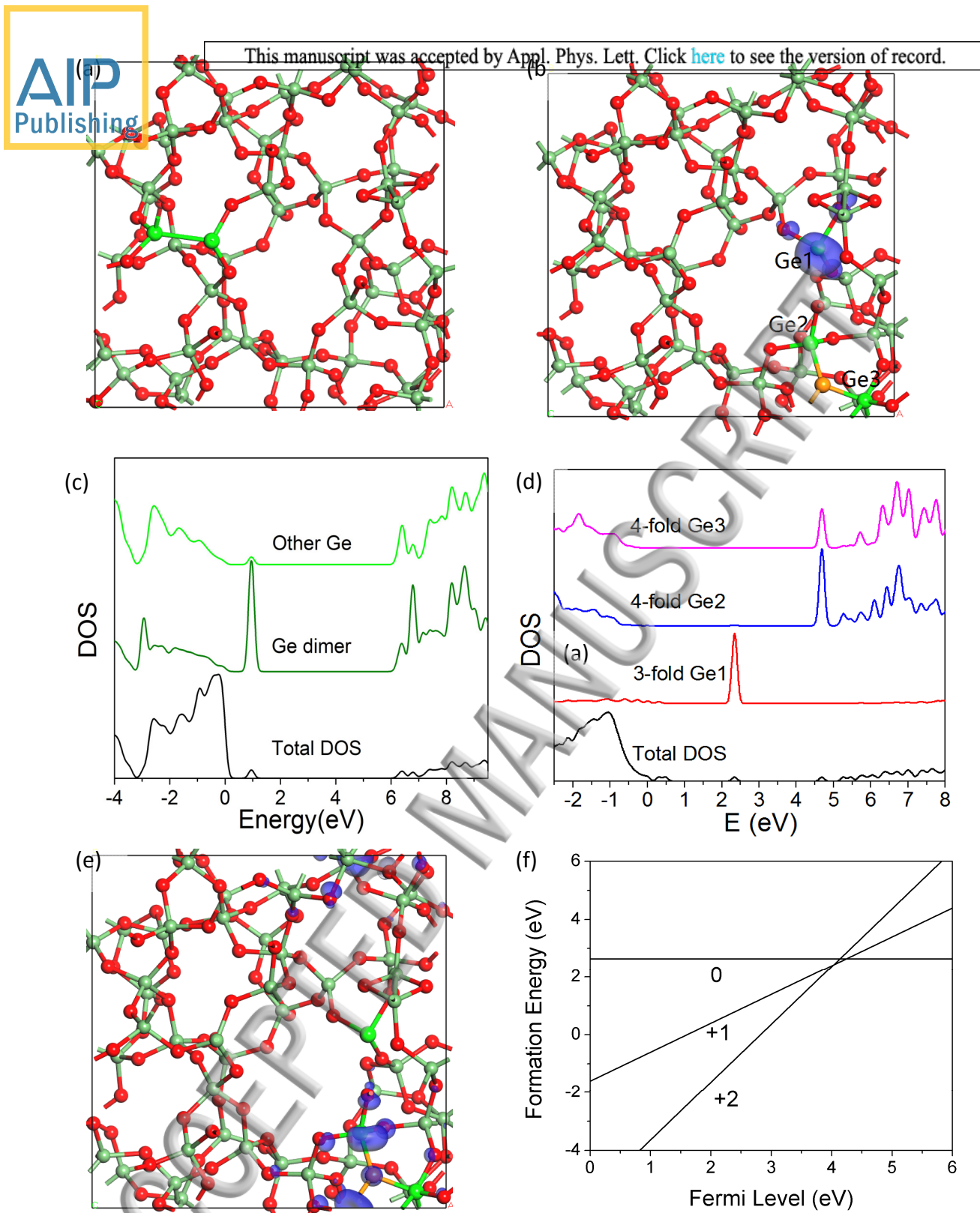


Fig 2

Energy(eV)

(a)

Ge

GeO₂

(b)

Ge

GeO₂

O vacancy
Ge-Ge states

VAP states

Fig. 3.

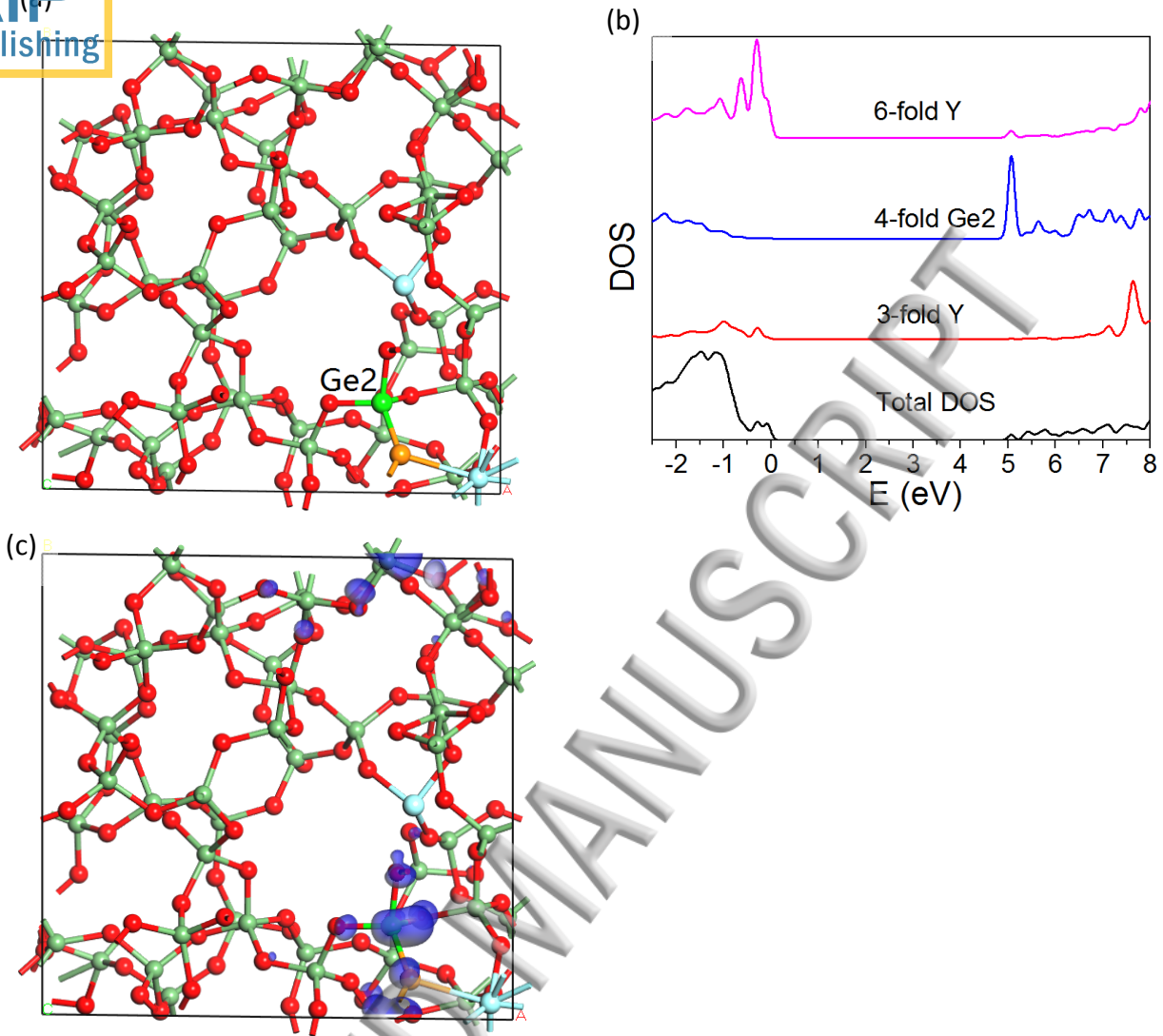


Fig. 4.

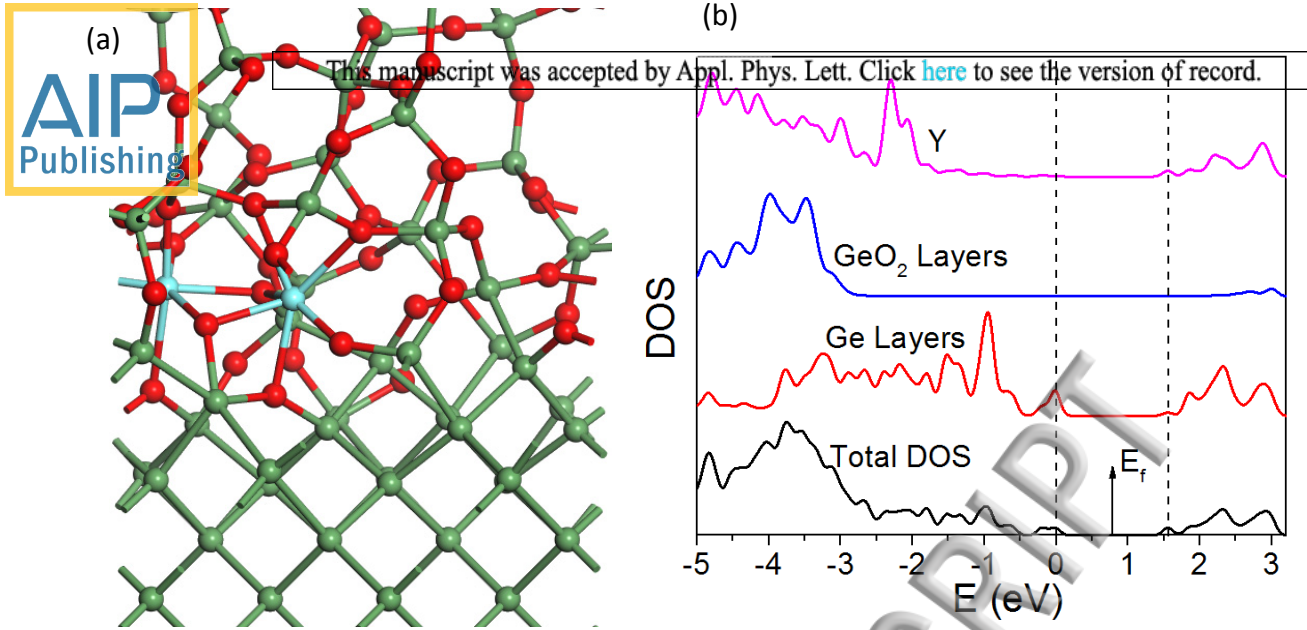


Fig 5.